Supporting Information

Vibronic Spectra of the *p*-Benzoquinone Radical Anion and Cation: A Matrix Isolation and Computational Study.

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Full quotation of Reference 43 (Gaussian program)

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford CT, 2010.

B3LYP/6-311+G(2d,p) cartesian coordinates of PBQ

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.000000	0.000000	1.438709
2	6	0.000000	1.267043	0.667870
3	6	0.000000	1.267043	-0.667870
4	6	0.000000	0.000000	-1.438709
5	6	0.000000	-1.267043	-0.667870
6	6	0.000000	-1.267043	0.667870
7	1	0.000000	2.177069	1.256376
8	1	0.000000	2.177069	-1.256376
9	1	0.000000	-2.177069	-1.256376
10	1	0.000000	-2.177069	1.256376
11	8	0.000000	0.000000	2.656604
12	8	0.000000	0.000000	-2.656604

Low freq.	-8.4805	-1.7853	-0.0011	-0.0010	-0.0008	8.8918

B3LYP/6-311+G(2d,p) cartesian coordinates of PBQ$^{\bullet-}$

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.000000	0.000000	1.465572
2	6	0.000000	1.219844	0.683154
3	6	0.000000	1.219844	-0.683154
4	6	0.000000	0.000000	-1.465572
5	6	0.000000	-1.219844	-0.683154
6	6	0.000000	-1.219844	0.683154
7	1	0.000000	2.149490	1.246991
8	1	0.000000	2.149490	-1.246991
9	1	0.000000	-2.149490	-1.246991
10	1	0.000000	-2.149490	1.246991
11	8	0.000000	0.000000	2.726726
12	8	0.000000	0.000000	-2.726726

Low freq.	-2.6665	0.0006	0.0006	0.0007	8.3816	17.8805

B3LYP/6-311+G(2d,p) cartesian coordinates of PBQ$^{\bullet+}$

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.000000	0.000000	1.444523
2	6	0.000000	1.288339	0.658885
3	6	0.000000	1.288339	-0.658885
4	6	0.000000	0.000000	-1.444523
5	6	0.000000	-1.288339	-0.658885
6	6	0.000000	-1.288339	0.658885
7	1	0.000000	2.187567	1.264322
8	1	0.000000	2.187567	-1.264322
9	1	0.000000	-2.187567	-1.264322
10	1	0.000000	-2.187567	1.264322
11	8	0.000000	0.000000	2.642429
12	8	0.000000	0.000000	-2.642429

Low freq.	-10.9031	-4.9197	-0.0006	-0.0005	0.0003	9.1984

results of TD-DFT calculations on $PBQ^{\bullet-}$ with B3LYP/6-311+G(2d,p)

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Excitation energies and oscillator strengths (SOMO = 29A):
leading configurations in blue, observed excited states in red

 Excited State   1:   ?Spin  -B1G    2.2280 eV  556.48 nm  f=0.0000
     27B -> 39B       -0.11193
     28B -> 29B        0.99887

 Excited State   2:   ?Spin  -AU     2.2476 eV  551.63 nm  f=0.0000
     27B -> 29B        1.00016
     28B -> 39B       -0.11287

 Excited State   3:   ?Spin  -B2U    3.0150 eV  411.22 nm  f=0.0459
     29A -> 30A        0.97326
     25B -> 39B       -0.10643

 Excited State   4:   ?Spin  -B1U    3.0393 eV  407.94 nm  f=0.0654
     26A -> 30A       -0.19714
     29A -> 35A        0.50035
     29A -> 38A        0.21502
     26B -> 29B        0.88932

 Excited State   5:   ?Spin  -B2G    3.2031 eV  387.07 nm  f=0.0000
     29A -> 31A        0.99911

 Excited State   6:   ?Spin  -B3G    3.2742 eV  378.68 nm  f=0.0000
     20A -> 30A        0.11079
     25A -> 30A       -0.20351
     26A -> 53A       -0.10759
     25B -> 29B        0.99315
     26B -> 32B        0.14141

 Excited State   7:   ?Spin  -AU     3.4264 eV  361.85 nm  f=0.0000
     29A -> 32A        1.00045

 Excited State   8:   ?Spin  -B3U    3.8870 eV  318.97 nm  f=0.0004
     29A -> 33A        0.99873

 Excited State   9:   ?Spin  -B1U    4.1731 eV  297.11 nm  f=0.1409
     26A -> 30A        0.59994
     29A -> 35A        0.71760
     21B -> 29B        0.10484
     25B -> 32B       -0.31325
     26B -> 29B       -0.23579

... followed be forbidden or very weak transition to 6 more states
above 250 nm.
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results of TD-DFT calculations on $PBQ^{\bullet+}$ with B3LYP/6-311+G(2d,p)

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Excited State   1:   ?Spin  -B1U    0.4638 eV 2673.48 nm  f=0.0159
     26A -> 29A       -0.41254
     25B -> 29B       -0.27819
     27B -> 28B        0.96808

... followed by 12 forbidden transitions above 260 nm amd a very
strong (and strongly mixed) one at 247 nm (f=0.1651)
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